Determination of Icing Inhibitors (Ethylene Glycol Monomethyl Ether and Diethylene Glycol Monomethyl Ether) in Ground Water by Gas Chromatography-Mass Spectrometry

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Received October 1, 2003

A gas chromatography/mass spectrometric assay method has been developed for the simultaneous determination of icing inhibitors, ethylene glycol monomethyl ether and diethylene glycol monomethyl ether in ground water contaminated with JP-8. Ethylene glycol monobutyl ether and ethylene glycol monoethyl ether were used as the internal standard and surrogate, respectively. 100 mL of ground water was extracted twice with 20 mL of methylene chloride. The extract was concentrated to dryness, dissolved with 100 μL of methanol and analyzed by GC-MS (SIM). The use of an Innowax column gave the peaks good chromatographic properties, and the extraction of these compounds from samples gave recoveries of about 50% with small variations. The method detection limits of the target compounds were in a range of 0.5-0.8 ng/mL in ground water.

Key Words : JP-8, Kerosene, Icing inhibitor, GC-MS, Fuel-type differentiation

Introduction

Ground water contamination caused by the accidental spill and leakage of fuel has been escalating in line with the growing consumption of energy. Recently, the U.S. Forces in Korea (USFK) and the Seoul Metropolitan Government have expressed confusion over the source of fuel contamination near Noksapyoung Subway Station in Seoul. One of the fuel types detected was in the family of kerosene-based fuels, such as JP-8 or kerosene. This led to an investigation into the differentiation between kerosene and JP-8.

Jet fuels have changed over time. Generally, JetA-1 is used for civil aircraft, except for propeller planes. JP-5 is used for carrier based navel aircraft; it has a high ignition point and is safer to handle and store. JP-8 is similar to JetA-1. During the Vietnam War, JP-5 presented many problems as a fuel for the air forces. Consequently, JP-8 was developed to overcome those problems.[1]

JP-8 formulations, kerosene-based mixtures of hydrocarbons, contain mandatory performance additives that are not usually blended with commercial jet fuel (Jet-A), which is generally manufactured mainly from straight-run kerosene.[2] JP-8 can therefore be described as kerosene containing three performance additives: icing inhibitor, antioxidants and antistatic compounds.[2] The detection of a specific additive of JP-8 in environmental samples can be an important clue to distinguish between kerosene and JP-8.

Ethylene glycol monomethyl ether (EGME) and diethylene glycol monomethyl ether (DEGME) are representative icing inhibitors which have a low octanol-water partition coefficient. The change in composition of EGME and DEGME in fuel occurs due to the loss of water-soluble icing inhibitors to water phase after an aviation fuel is released into the environment. To trace the environmental fate of icing inhibitors in jet fuel, therefore, requires a trace analysis method of ether-type antioxidants in ground water.

To date, several analytical methods for the determination of EGME and DEGME in aviation fuels have been described.[3,4] The standard test method describes the detection with a refractometer after extraction with water.[3] Bernabei[4] determined two anti-icing additives in jet fuel based on a gas-chromatographic technique using a mass spectrometer without sample pre-treatment. But these methods are not applicable to the detection of trace EGME and DEGME in ground water. The quantitative methods of ethylene glycol in the environment[5,6] or biological samples[7] are performed. But there is no method analyzing EGME and DEGME in ground water contaminated with JP-8.

Our aim was to develop an analytical method that allows the simultaneous quantification of trace EGME and DEGME in groundwater contaminated with aviation fuels at the low-ng/mL level. The target compounds were extracted with methylene chloride by salting-out with sodium chloride.

Experimental Section

Chemicals and reagents. Ethylene glycol monomethyl ether (EGME), ethylene glycol monoethyl ether (EGEE), diethylene glycol monomethyl ether (DEGME) and ethylene glycol monobutyl ether (2-butoxy ethanol, EGBE) were purchased from Aldrich (Milwakee, USA). Analytical grade sodium chloride (Junsei, Dongkeung, Japan) was used as the salting-out reagent, and *n*-hexane, acetone, acetonitrile and methanol (J.T. Baker, Phillipsburg, USA) were used as solvents. Water was purified in Milli-Q (Millipore Corp., Milford, MA).

Spiking. Spiked samples were prepared by Milli-Q water (100 mL) with 10-100 μL of standard solutions at a concentration of 50-5000 ng/mL and with 20 μL of the solution

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containing internal standards at a concentration of 2000 ng/mL.

Extraction procedure. In a 250-mL separating funnel was placed100 mL of the ground water sample. About 30 g of NaCl and 50 μL of EGBE internal standard solution and EGEE surrogate standard solution (2.0 μL/mL in methanol) were added to this solution, and the sample was extracted twice with 20 mL of methylene chloride by mechanical shaking for 10 min for each extraction. The organic phase was evaporated in a vacuum rotary evaporator and dried finally under a nitrogen stream to about 100 μL volume. The solution was transferred into a V-shape auto vial. At appropriate times, a 2 μL sample of the solution was analyzed by GC.

Gas chromatography-mass spectrometry. All mass spectra were obtained with an Agilent 6890 gas chromatograph and 5973 N-type mass selective detector. The ion source was operated in the electron ionization mode (EI; 70 eV, 230 °C). Full-scan mass spectra (m/z 40-800) were recorded for the identification of analytes at high concentration. Confirmation of trace chemicals was completed by two MS characteristic ions, the ratio of two MS characteristic ions and GC-retention time matches to those of the known standard compounds. The ions selected in this study and the operating parameters of GC-MS are given in Table 1.

Calibration and quantification. Calibration curves for EGME and DEGME were established by extraction after adding 0.5, 2.5, 10, 100, 250 and 500 ng of standards and 100 ng of internal standard to 50 mL of kerosene. The ratio of the peak area of standard to that of internal standard was used in the quantification of the compound.

Results and Discussion

Chromatography. For the GC separation of EGME and DEGME, the use of Innowax was found to be efficient. The chromatograms are shown in Figure 1. As can be seen from the figure, the peaks of EGME, DEGME and internal standard are symmetrical and separation of the analytes from the background compounds in samples is very good. The retention times of EGME and DEGME were 5.24 and 9.45 min.

Table 1. GC-MS conditions for the determination of the target compounds

Parameter	Condition			
Column	Innowax, 30m × 0.25 mm I.D. × 0.25 μm F.T			
Carrier	He at 1.0 mL/min			
Oven Temp.	10 °C/min 40 °C → 180 °C (1 min)		post run 250 °C (3 min)	
Split Ratio	1 : 10			
Injector Temp.	260 °C			
Transfer Temp.	280 °C			
Selected Ion Group	Group	Start Time (min)	Compound	Selected Ions, m/z
	1	4.50	EGME	31, 59, 72
	2	7.50	ISTD	45, 57, 87
	3	9.00	DEGME	45, 59, 90

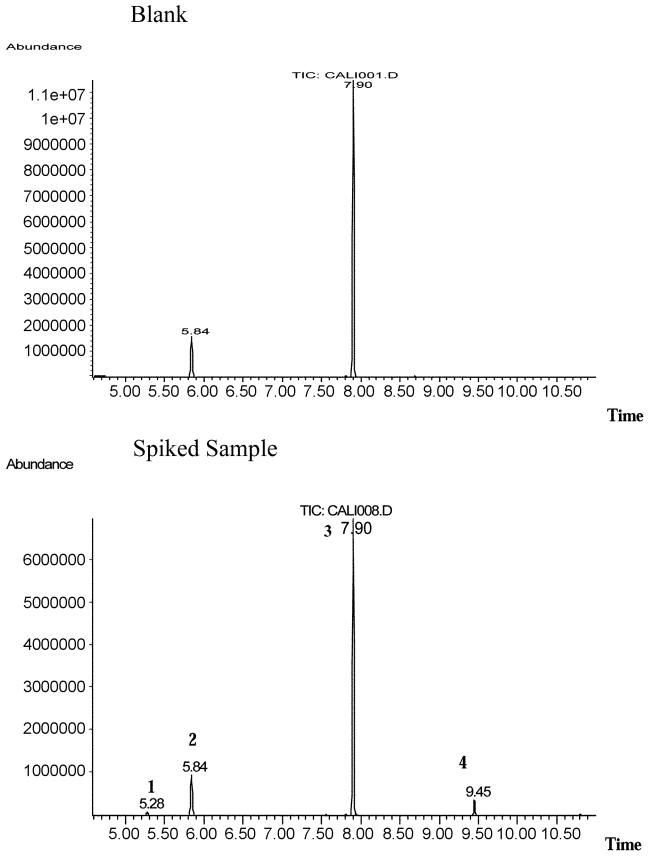

Figure 1. Chromatograms of the extracts from milli-Q water (blank) and milli-Q water spiked with 80 ng/mL of standards. (1=EGME, 2=EGEE, 3=EGBE, 4=DEGME).

Mass spectrometry. The mass spectra of EGME, EGEE, EGBE and DEGME are shown in Figure 2. EGME shows the molecular ion at m/z 76 and the base peak at m/z 45, and the diagnostic ions at m/z 31, 43, 47 and 58. EGEE shows the molecular ion at m/z 90 and the base peak at m/z 59, and the diagnostic ions at m/z 31, 43, 45 and 72. DEGME has the major peak at m/z 45 and the diagnostic ions at m/z 31, 59, 75, 89 and 90, and EGBE, the base peak at m/z 57 and the diagnostic ions at m/z 31, 45, 71, 75 and 87.

Extraction and clean up. The optimization of the whole procedure resulted in reproducible purification and concentration of EGME and DEGME from ground water samples. Relative high recoveries were achieved by adding a large amount (above 5 g) of sodium chloride. Until now, it was thought impossible to extract the compounds from water matrix to organic solvent due to their low octanol-water partition coefficients. Test samples at 2.0 and 20.0 ng/g were prepared and the relative recovery was calculated by the percentage of the analytes recovered. The recoveries of the test compounds were about 50 %, as shown in Table 2.

Linearity and detection limits. Examination of a typical standard curve by computing a regression line of peak area ratios of EGME and DEGME to the internal standard on concentration, using a least-squares fit, demonstrated a linear relationship with correlation coefficients being greater than 0.998 (Table 3).

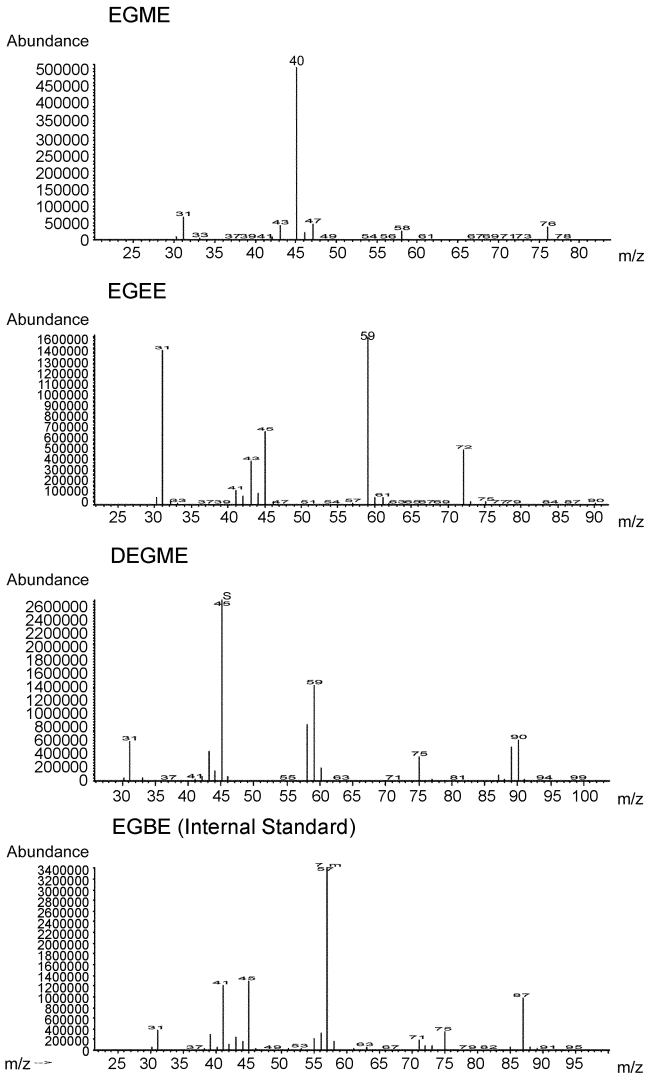

Figure 2. Mass spectra of EGME, EGEE, DEGME and EGBE.

Table 2. Recoveries of the target compounds from water (n = 5)

Compounds	Amount spiked (ng/mL)	Recovery (%) ± RSD (%)
EGME	5.0	56.2 ± 4.7
	20.0	51.2 ± 5.3
DEGME	5.0	54.0 ± 9.0
	20.0	48.6 ± 10.3

Detection limits of EGME and DEGME were found to be 0.8 and 0.5 ng/mL based upon an assayed sample of 100 mL (Table 3). Detection limits were defined by a minimum signal-to-noise ratio of 3 and coefficients of variation for replicate determinations (n=5) of 15% or less of the extract of sample.

Table 4. Precision and accuracy of target compounds in water (n = 5)

Compounds	Amount spiked (ng/mL)	Results
		X ± SD (RSD%)
EGME	2.0	2.1 ± 0.2 (7.6%)
	10.0	9.8 ± 0.4 (3.8%)
DEGME	2.0	2.0 ± 0.2 (10.9%)
	10.0	8.7 ± 0.1 (1.3%)

X = mean value (ng/mL); SD = standard deviation; RSD = relative standard deviation (%)

Precision and accuracy. The range and standard deviation values for precision and accuracy are given in Table 4. For five independent determinations at 2.0 and 10.0 ng/g, the coefficient of variation was less than 11%.

Conclusions

The peaks of EGME and DEGME have good chromatographic properties with the use of an Innowax column and show sensitive response for the EI-MS (SIM). An analytical procedure for the target compounds with a range of method detection limits of 0.5-0.8 ng/mL was established.

Although kerosene based-fuel has been found around Noksapyoung Subway Station, it is difficult to identify whether its exact fuel type is kerosene or JP-8, because JP-8 has the same hydrocarbon pattern as kerosene. Identification of the specific additive of JP-8 found in this area can be a clue to the source of the kerosene based-fuel contamination. The method we developed here may be very valuable in understanding the contamination source of the spilled fuel.

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Table 3. Linearity and detection limits of the target compounds

Compounds	Detection Range (ng/mL)	No of points	Linear equation	Linearity	Method Detection Limit (ng/mL)
EGME	1.0-40	6	Y = 0.0052x + 0.0029	0.9984	0.8
DEGME	1.0-40	6	Y = 0.0046x + 0.0017	0.9980	0.5

X = the analyte concentration (ng/mL); Y = the peak area ratio of the analyte to internal standard.